A Study of the Ligand Exchange of Bromo(*o*-tolyl)bis(triphenylphosphine)nickel(II) with Amine by Means of ^{31}P- and ^{13}C-NMR Spectroscopy

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The amine substitution of bromo(*o*-tolyl)bis(triphenylphosphine)nickel(II) was investigated by the use of ^{31}P- and ^{13}C-NMR. The triphenylphosphine ligands are readily replaced by sterically less crowded amines, such as primary amines, secondary amines, pyridine, and *γ*-picoline, at room temperature in chlorobenzene, while no replacement at all takes place with tertiary amines. The equilibrium constants with *γ*-picoline, pyridine, or dibutylamine, as defined by Eq. 2, show that the entropy change contributes predominantly to the constant. The substitution with pyrrolidine, as monitored by means of ^{13}C-NMR, indicates that the amine coordinates to the nickel(II) atom.

It is well known that organo transition-metal complexes are stabilized by the coordination of the tertiary phosphine ligand to the metal atoms. For example, halogeno(aryl)bis(triphenylphosphine)nickel(II), first prepared by Chatt[1] twenty years ago, is quite stable in organic solvents. This compound acts as a precursor to an active catalyst for the selective dimerization and codimerization of olefin[2-4] and gives a cationic nickel(II) complex with an amine ligand on treatment with $AgClO_4$.[5] Little attention has, however, been paid to organo transition-metal complexes with amine ligands, presumably because they are too unstable to be easily isolated and characterized. Little information is, accordingly, available with respect to the coordination states of amines, although amine is expected to behave much like phosphine.

Triphenylphosphine ligands on bromo(*o*-tolyl)bis(triphenylphosphine)nickel(II) are readily replaced by other tertiary phosphines, with the driving force for the replacement being steric in nature.[6] The same procedure may be extended to the substitution of amine for phosphine. Thus, the substitution reactions of various amines, as represented by:

$$[NiBr(o\text{-tolyl})(PPh_3)_2] \underset{PPh_3}{\overset{amine}{\rightleftharpoons}} [NiBr(o\text{-tolyl})(amine)(PPh_3)] \underset{PPh_3}{\overset{amine}{\rightleftharpoons}} [NiBr(o\text{-tolyl})(amine)_2] \quad (1)$$

have been investigated in order to elucidate the nature of the amine coordination.

Experimental

Materials. Bromo(*o*-toly)bis(triphenylphosphine)nickel(II) was prepared by the oxidative addition of *o*-bromotoluene to tetrakis(triphenylphosphine)nickel(0) according to the literature.[7]

All the experiments were conducted under a nitrogen atmosphere. Chlorobenzene which has been dried by P_2O_5 before distillation was used as the solvent. No reaction of chlorobenzene with amines was observed under the present experimental conditions. The pyridine, *γ*-picoline, pyrrolidine, piperidine, butylamine, and dibutylamine were dried by CaH_2 before distillation. The other amines, such as quinoline, 4-methoxyaniline, 3,4-dimethylaniline, 4-methylaniline, aniline, 4-chloroaniline, *N*-methylpyrrolidine, *N*-methylpiperidine, tributylamine, t-butylamine, propylamine, dipropylamine, and *N,N,N',N'*,-tetramethylethylenediamine, obtained from commerical sources, were used without further purification.

Procedures. All the samples were prepared under a nitrogen atmosphere. To bromo(*o*-tolyl)bis(triphenylphosphine)nickel(II) (50 mg) placed in a two-necked flask (20 ml) are added chlorobenzene (5.00 ml) containing a known amount of an amine, the solution was then stirred at room temperature for about 1 h before ampouling the solution with C_6D_6 (D-lock) and TMS into a NMR tube (10 mm. O.D.).

The ^{31}P- and ^{13}C-NMR spectra were obtained on a Japan Electron Optics Laboratory FX-100 spectrometer operating the pulsed Fourier transform mode at 40.26 and 25.00 MHz, the repetitions being 6 s (^{31}P-; 400—1000 pulses) and 2 s (^{13}C-; 10000—35000 pulses). The ^{31}P-NMR spectra were taken without proton-decoupling, if necessary. The ^{31}P- and ^{13}C-NMR chemical shifts were reported in ppm, downfield from internal triphenylphosphine (−5.86 ppm from H_3PO_4) and TMS respectively.

Results and Discussion

General Features of the Substitution. Figure 1 shows the ^{31}P-{^{1}H}NMR spectra of the chlorobenzene solutions of *trans*-[NiBr(*o*-tolyl)$(PPh_3)_2$] (to be denoted by the M-complex here after) and pyridine (pK_b= 8.8) at −20 °C. The increase in the molar ratio of pyridine to the nickel complex results in a decrease in the intensity of resonance, S_0, at 29.4 ppm due to the M-complex, accompanied by an increase in that of the resonance, L_p, at 0 ppm due to free triphenylphosphine. The resonance, S_1, at 36.9 ppm can be attributed to the monosubstituted M-complex with pyridine, [NiBr(*o*-tolyl)(pyridine)(PPh_3)].

The degree of amine coordination to nickel is represented by the relative intensities, h_p and h_1, of L_p and S_1 the resonances:

$$h_p = \frac{h(L)_p}{h(L_p)+h(S_0)+h(S_1)}, \quad h_1 = \frac{h(S_1)}{h(L_p)+h(S_0)+h(S_1)},$$

where $h(L_p)$, $h(S_0)$, and $h(S_1)$ are the peak heights of the resonances for free triphenylphosphine, the M-complex, and the monosubstituted M-complex respectively.

With respect to the amines with a pyridine ring, the following coordination sequence may be deduced from

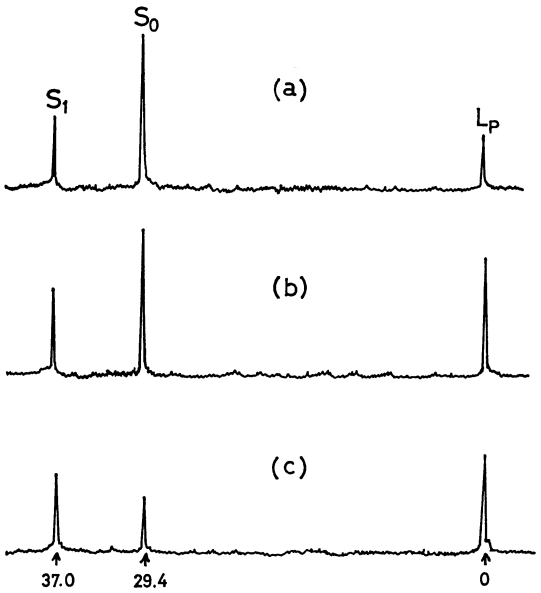

Fig. 1. ^{31}P-{^1H} NMR spectra in the substitution of M-complex with pyridine at −20 °C at the molar ratio of $[pyridine]_0/[M]_0=5$(a), 10(b), or 20(c).

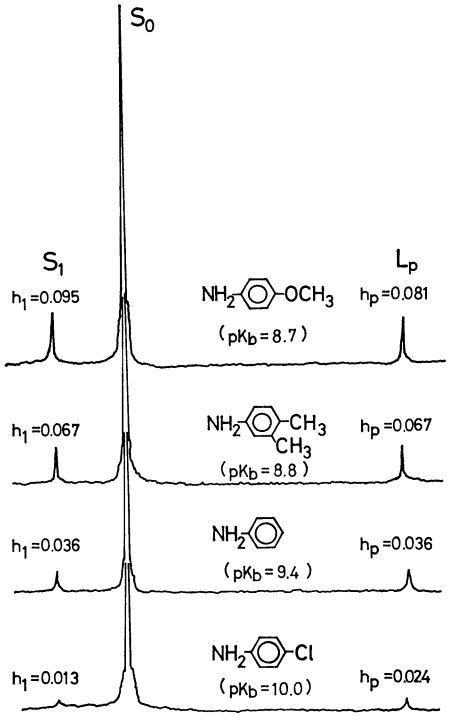

Fig. 2. ^{31}P-{^1H} NMR spectra in the substitution of M-complex with substituted aniline at the molar ratio of $[aniline]_0/[M]_0=20$ at −20 °C.

the relative intensities at −20 °C;

$$\underset{(pK_b=7.9)}{\gamma\text{-picoline}} > \underset{(pK_b=8.8)}{\text{pyridine}} \gg \underset{(pK_b=9.2)}{\text{quinoline}}$$

where the molar ratio of the amine to the M-complex is 10. This sequence appears to imply that the more basic the amine, the stronger the coordination. In order to confirm this tendency, *p*-substituted anilines with equal steric crowding were chosen as the substitutes.

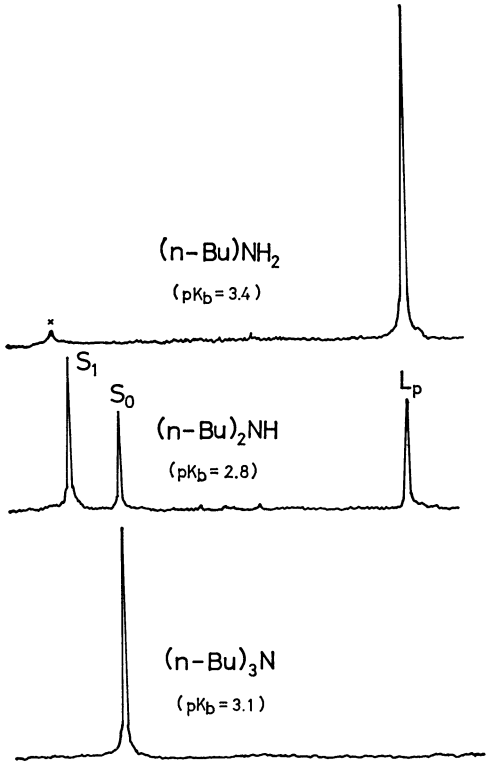

Fig. 3. ^{31}P-{^1H} NMR spectra in the substitution with $NH_{3-n}(n\text{-Butyl})_n$($n=1$, 2, and 3) at molar ratio of $[amine]_0/[M]_0=6$ at −20 °C.

The ^{31}P-{^1H} NMR spectra of the M-complex p-substituted aniline system are shown in Fig. 2. The stronger electron donor results in the higher relative intensities, h_p and h_1, of the free triphenylphosphine and the monosubstituted M-complex.

On the other hand, most of the triphenylphosphine on M-complex is replaced by butylamine ($pK_b=3.4$) at the molar ratio of [butylamine]/[M]=6, while no replacement by tributylamine ($pK_b=3.1$) takes place at all, as is shown in Fig. 3. Essentially the same sequence was observed with mono-, di-, and tripropylamines. Other sterically crowded amines, such as *N*,*N*-dimethylaniline, *N*-methylpyrrolidine, and *N*-methylpiperidine, gave neither the resonance due to free triphenylphosphine nor that due to the monosubstituted M-complex. From comparisons of the ^{31}P-NMR spectra (Fig. 1) with pyridine ($pK_b=8.8$) and (Fig. 3) with butylamine ($pK_b=3.4$), it seems that the triphenylphosphine on the M-complex is replaced more readily by a strong amine base. Figure 3 clearly shows that the steric factor is predominant in the substitution with amine, as well as with other tertiary phosphine ligands.[6]

When *N*,*N*,*N*′,*N*′,-tetramethylethylenediamine was used, both L_p and S_0 resonances were observed, while no S_1 resonance corresponding to the monosubstituted M-complex was detected, suggesting some chelation of the diamine, although no further study was done.

The ^{31}P- chemical shifts (S_1) of the monosubstituted M-complex with various amines, [NiBr(*o*-tolyl)(amine)(PPh_3)], were almost the same (independent of the strength of the amine base): 34.7 ppm ($NH(n\text{-}Pr)_2$),

TAELB 1. EQUILIBRIUM CONSTANTS WITH AMINE; $K_1=\frac{[S_1][L_p]}{[S_0][L_N]}$

Amine	$[N]_0/[M]_0$	K_1 24 °C	10 °C	0 °C	−10 °C	−20 °C
$NH(n\text{-Bu})_2$	1.53	0.71	—	0.48	—	0.48
	3.07	0.80	0.60	0.55	0.59	0.55
	mean	0.75	0.60	0.51	0.59	0.51
Pyridine	5.0	0.21	0.23	0.24	0.27	—
	10.0	0.24	0.22	0.19	—	—
	mean	0.23	0.23	0.22	0.27	—
γ-Picoline	3.0	0.85	0.78	0.69	0.51	—
	6.0	0·79	0.72	0.61	0.61	—
	mean	0.82	0.75	0.65	0.57	—

34.4 ppm ($NH(n\text{-Bu})_2$), 36.5 ppm (pyrrolidine), 36.7 ppm (piperidine), 37.2 ppm (γ-picoline), and 36.9 ppm (pyridine).

Evaluation of Equilibrium Constant. Since substituted M-complexes with amines were too unstable to be isolated, we attempted to evaluate the equilibrium constants of Eq. 2 using pyridine, γ-picoline, or dibutylamine in order to confirm Eq. 2.

The concentrations of free triphenylphosphine, the M-complex, and the monosubstituted M-complex at equilibrium can be calculated from the relative peak areas of ^{31}P-NMR (without ^1H-decoupling) and from the initial concentrations of the M-complex and the amine, because they are proportional to the concentrations (mol/l), $[L_p]$, $[S_0]$, and $[S_1]$. The relative peak areas are as follows:

$$\underset{[S_0]}{[NiBr(o\text{-tolyl})(PPh_3)_2]} + \underset{[L_N]}{Amine} \underset{\text{in } C_6H_5Cl}{\overset{K_1}{\rightleftarrows}} \underset{(cis \text{ and } trans)}{\underset{[S_1]}{[NiBr(o\text{-tolyl})(amine)(PPh_3)]}} + \underset{[L_p]}{PPh_3} \quad (2)$$

$HL_p=H(L_p)/(H(S_0)+H(S_1)+H(L_p))$, $HS_0=H(S_0)/(H(S_0)+H(S_1)+H(L_p))$, and $HS_1=H(S_1)/(H(S_0)+H(S_1)+H(L_p))$, where $H(L_p)$, $H(S_0)$, and $H(S_1)$ are the peak areas of the resonances of L_p, S_0, and S_1 recorded on ^{31}P-NMR charts. Each concentration is a function of HL_p, HS_1, or HS_3, as represented by Eqs. 3—7.

$$[L_p] = 2[M]_0 \times HL_p \quad (3)$$

$$[S_0] = [M]_0 \times HS_0 \quad (4)$$

$$[S_1] = 2[M]_0 \times HS_1 \quad (5)$$

$$[S_2] = [M]_0 - [S_0] - [S_1] \quad (6)$$

$$[L_N] = [N]_0 - 2[S_2] - [S_1] \quad (7)$$

$[M]_0$ is the total concentration of nickel(II) complex and is given by the amount of M-complex initially charged, and $[N]_0$ is the concentration of amine initially charged. $[S_2]$ and $[L_N]$ are the concentrations of the disubstituted M-complex and the free amine at equilibrium respectively.

The equilibrium constants $K_1=\left(\frac{[S_1][L_p]}{[S_0][L_N]}\right)$ thus obtained at different values of $[N]_0/[M]_0$ are summarized in Table 1. Despite the two-fold change in $[N]_0/[M]_0$ the values of K_1 are almost constant at any temperature, as was expected.

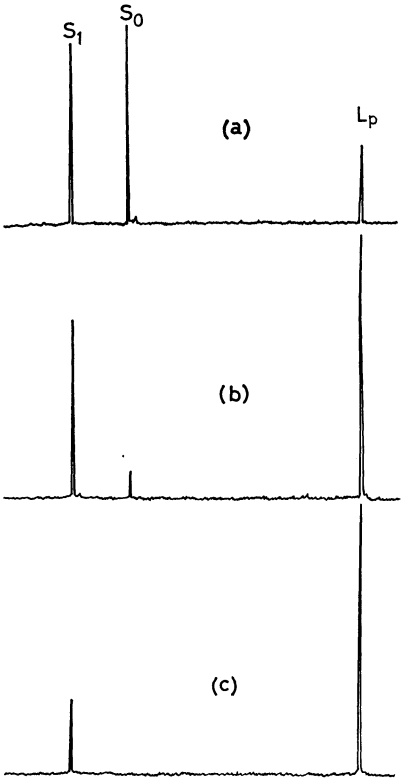

Fig. 4. ^{31}P-{^1H} NMR spectra in the substitution of M-complex with pyrrolidine at the molar ratio of 1(a), 2(b), or 4(c) at −24 °C.

It is notable that the effect of the temperature on K_1 is very small, indicating that the entropy change is the predominant factor in the equilibrium constant. This feature is in accord with the fact that bulky amines do not result in the substitution. On the other hand, the equilibrium constants for sterically less crowded amines, such as propylamine, butylamine, pyrrolidine, and piperidine, appear to be too large, rendering the evaluation difficult because of the difficulty in evaluating the value of $[L_N]$, even in a system with added PPh_3. They are, however, presumably one order of magnitude larger than that for γ-picoline. It may be imagined that more than two molecules of a sterically less crowded amine coordinate to the nickel(II) atom, whereas no new resonance in ^{31}P-{^1H} NMR was observed in addition to the S_0, S_1, and L_p resonances,

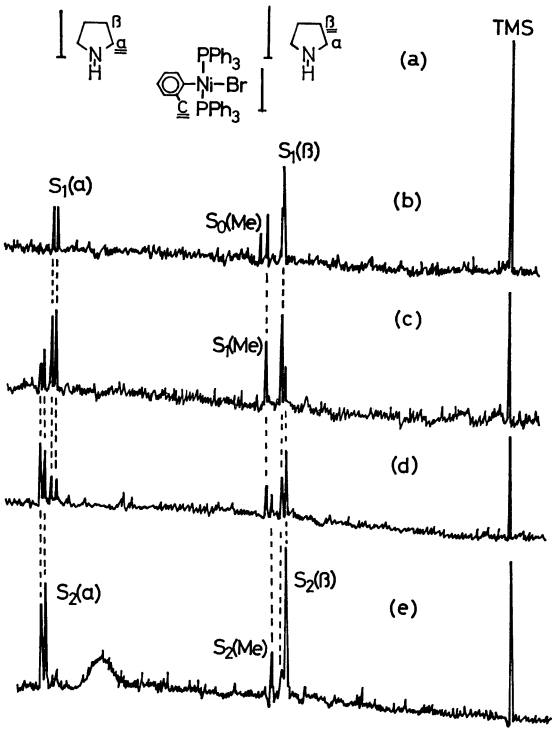

Fig. 5. ^{13}C-{^1H} NMR spectra in the substitution of M-complex with pyrrolidine at the molar ratio of 1(b), 2(c), 4(d), and 8(e), and free pyrrolidine(a) at −20 °C.

as is shown in Figs. 1—4, giving no indication of such coordination.

Evidence of Amine Coordination Obtained by Means of ^{13}C-{^1H} NMR. More direct evidence for the coordination of amine to the nickel(II) atom will be provided by ^{13}C-{^1H} NMR. Pyrrolidine was selected as the candidate amine, because it has only two kinds of carbon atoms exhibiting a strong coordination ability to the nickel(II) atom, thus making the ^{13}C-{^1H} NMR analysis simpler. The results are shown in Fig. 5. The methyl carbon (26.27 ppm, $S_0(Me)$) of the M-complex and the α-carbon (47.12 ppm, $L_N(\alpha)$) and the β-carbon (25.78 ppm, $L_N(\beta)$) of free pyrrolidine are observed in the range of 0—50 ppm, as is shown Fig. 5(a).

In Fig. 5(b) for $[N]_0/[M]_0=1$, the α-carbon of the pyrrolidine ligand of the monosubstituted M-complex is split into two resonances (47.56 ppm and 48.00 ppm, $S_1(\alpha)$), while the β-carbon is shifted to 23.98 ppm (broad)($S_1(\beta)$), and the methyl carbon, to 25.58 ppm ($S_1(Me)$). In Fig. 5(c) for $[N]_0/[M]_0=2$, three new resonances are observed. The two resonances at 49.17 ppm and at 48.82 ppm ($S_2(\alpha)$) are due to the α-carbon of pyrrolidine of the disubstituted M-complex, while the other at 23.54 ppm (broad)($S_2(\beta)$), is that of the β-carbon.

It should be noticed that the resonance at 26.27 ppm ($S_0(Me)$) observed in Fig. 5(b) mostly disappears in Fig. 5(c). In Fig. 5(d) for $[N]_0/[M]_0=4$, one new resonance (25.00 ppm, $S_2(Me)$) is detected; it can be assigned to the methyl carbon of the disubstituted M-complex. The relative intensities of the $S_2(\alpha)$ and $S_2(\beta)$ resonances are larger than those in Fig. 5(d).

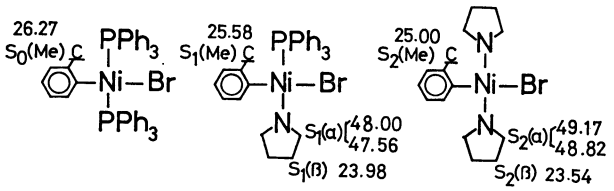

Fig. 6. Assignment of ^{13}C-{^1H} NMR.

This change in the ^{13}C-NMR spectra with the amine concentration is in accord with the results for ^{31}P-{^1H} NMR shown in Fig. 4.

The assignment of these ^{13}C-{^1H} NMR resonances is summarized in Fig. 6. The assignment is based on the following facts; 1) three resonances ($S_0(Me)$, $S_1(Me)$, and $S_2(Me)$) are observed, with their relative intensities depending reasonably on the molar ratio of pyrrolidine, and 2) the intensities of $S_2(\alpha)$ and $S_2(\beta)$ relative to $S_1(\alpha)$ and $S_1(\beta)$ increase with the increase in the molar ratio of pyrrolidine. Since the ^{13}C-resonances ($S_1(\alpha)$ and $S_2(\alpha)$) of the α-carbons of pyrrolidine are observed to split into two peaks upon coordination to nickel(II), it may be suggested that this is a mixture of *cis-* and *trans-* forms of mono- and disubstituted M-complexes, although only one resonance of the ^{31}P-{^1H} NMR spectra is observed with the monosubstituted M-complex (Fig. 4). It is also possible that no rotation is allowed about the N–Ni bonds of the substituted M-complexes, thus resulting in the split. No clear explanation of the split can, however, be made at present.

At a high molar ratio of pyrrolidine (Figs. 5(d) and 5(e)), no resonance due to free pyrrolidine (25.78 ppm (α) and 47.12 ppm (β)) is detected, while a broad resonance is observed in the range from 39 to 45 ppm (Fig. 5(e)). This resonance remains unclarified. Free pyrrolidine is possibly polymerized during the ^{13}C-{^1H} NMR measurements (about 10 hours at room temperature for each measurement) because of its reactivity is higher than that of the coordinated pyrrolidine.

It may be concluded at least that the driving force for the substitution is predominantly the steric factor of amine rather than the electronic factor, as is the case with the substitution of triphenylphosphine ligands with other tertiary phosphines.

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